The Crystal Structure of Linarite, $PbCu(SO_4)(OH)_2$

By

Takaharu ARAKI

Geological and Mineralogical Institute, University of Kyoto

(Received July 21, 1958)

Abstract

The lattice constants of the crystal of linarite from Kisamori are $a=9.67$, $b=5.64$, $c=4.68$Å and $\beta=102°40'$. Its space group is $P2_1/m$, and there are two molecules per unit cell.

Intensity data were obtained through the oscillation photographing, and the structure was determined by means of the two-dimensional Patterson, Fourier and difference syntheses.

Introduction

There are many secondary minerals whose crystal structures were not yet analysed. For example, a number of sulfates containing iron or copper are of the case.

On linarite from Red Gill, Cumberland, England, only an X-ray study has been reported by L. G. BERRY (1951) giving the lattice constants, space group and the structure formula.

Linarite, a basic sulfate of lead and copper, $PbCu(SO_4)(OH)_2$, occurs widespreadly in small amount as a secondary mineral in oxidized zones of the copper and lead deposits.

Recently the writer has examined the results of BERRY and determined further the structure of the mineral.

Experimental

Specimens from Kisamori mine, Akita prefecture, Japan were used in this investigation. They are prismatic and elongated along b-axis. The unit cell dimensions were obtained measuring the distances between the layer lines on rotation photographs taken with $CuK\alpha$ radiation. The result is :

$$a = 9.67 \pm 0.02\,\text{Å},\ \ b = 5.64 \pm 0.01\,\text{Å},\ \ c = 4.68 \pm 0.01\,\text{Å},\ \ \beta = 102°40' \pm 15'\ \text{(goniometric)}$$

Density was measured pycnometrically and 5.34 was obtained. Therefore, there are two chemical units in the unit cell. The space group is $P2_1/m$, $0k0$ reflexions being present only when $k = 2n$ and the mineral having holohedral symmetry morphologically. These results are in good agreement with those previously reported.

The intensity data were obtained, using multiple film technique, by oscillation photographs taken with $CuK\alpha$ radiation and each of the intensities was estimated visually with the aid of a graded intensity scale. The usual corrections for Lorentz and polarization factors were applied and the set of numbers thus obtained were converted to the absolute scale applying the Wilson's method to each of the intervals divided for $\sin\theta/\lambda$, but the corrections for the absorption and temperature factors were neglected. These numerical values thus derived were assumed to be the observed structure factors.

The structure determination

In the space group $P2_1/m$, equivalent positions are

$4(f)$ $\pm|x, y, z; \bar{x}, 1/2+y, \bar{z}|$ $2(e)$ $\pm|x, 1/4, z|$

$2(d)$ $1/2, 0, 1/2; 1/2, 1/2, 1/2$. $2(c)$ $0, 0, 1/2; 0, 1/2, 1/2$.

$2(b)$ $1/2, 0, 0; 1/2, 1/2, 0$. $2(a)$ $0, 0, 0; 0, 1/2, 0$.

In the Patterson maps it is considered that prominent peaks represent $Pb-Pb$ and $Pb-Cu$ vectors and less prominent are $Pb-S$, $Cu-Cu$ and $Pb-O$ vectors. Provided that Pb and Cu atoms occupy the positions of $2(e)$ respectively, a $Pb-Pb$ vector must appear at $2x, 1/2, 2z$ and $Pb-Cu$ vectors at $y=0$ and $y=1/2$. But if Cu atoms occupy a set of centers and Pb atoms the positions of $2(e)$, $Pb-Cu$ vectors must appear at $y=1/4$.

At the first step of the determination of atomic parameters, two-dimensional Patterson syntheses were carried out using observed $F^2(hk0)$, $F^2(0kl)$ and $F^2(h0l)$ terms respectively.

In the Patterson maps which are shown in Fig. 1, there are prominent peaks of different height, i.e. the heighest at $y=1/2$ and the second at $y=1/4$. Comparing the peak height of these vectors with that of the origin one and also considering the weights of the vectors, it was inferred that the heighest peak at $y=1/2$ represents a $Pb-Pb$ vector and the second at $y=1/4$ a $Pb-Cu$ vector. Therefore the approximate atomic parameters of Pb atoms were easily obtained as $x=0.160$, $y=1/4$, $z=0.170$, from the Patterson maps projected on the (001) and (100) planes, and taking its coordinates of equivalent positions into account.

Further, it was found that the $Pb-Cu$ vector at $y=1/4$ locates just at $1/2-x, 1/4, 1/2-z$, where x and z are the approximate parameters of Pb atoms. Consequently it was deduced that Cu atoms are situated at the centers, $2(d)$. In the Patterson map projected on the (010) plane there appeared only a prominent peak which could be regarded to be an overlap of the $Pb-Pb$ and $Pb-Cu$ vectors. This fact will confirm the deduction above mentioned. Therefore, the space group of linarite was also determined to be $P2_1/m$ from the interpretation of the Patterson maps. The other interatomic vectors could, however, hardly be recognized due to the background in the Patterson maps.
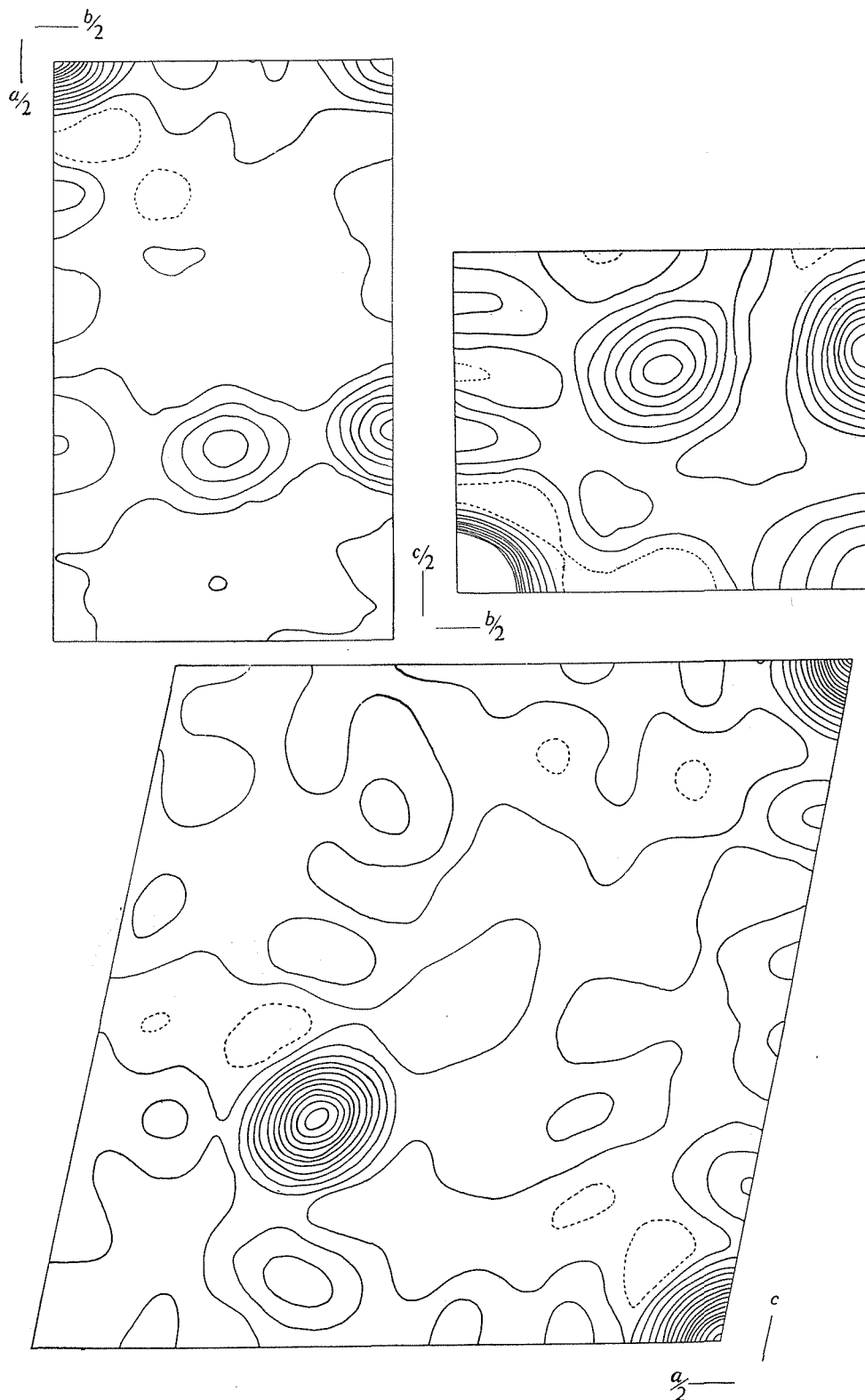
Fig. 1. The Patterson maps projected on the (001), (100) and (010) planes respectively. Contours at an arbitrary unit.

From the parameters for the heavy atoms above obtained the signs of F_0's whose values were relatively large were easily found taking the contribution of the heavy atoms to the structure factors into account.

At the outset, the electron densities on the (001) and (010) planes were evaluated by means of the two-dimensional Fourier syntheses with F_0's whose signs could be determined, and the maxima in the electron density maps which represent the positions of Pb atoms were found at the positions close to the approximate positions obtained through the foregoing Patterson syntheses, whereas Cu atoms just at the centers. Furthermore, the maxima which are regarded to be the positions of S atoms were found, but the Fourier syntheses failed to resolve the positions of O atoms and OH groups.

The coordinates of O atoms and OH groups were then assumed keeping the heavy atoms and S atoms in their positions above mentioned respectively and two-dimensional Fourier summations were carried out using F_c's at the intervals of 1/60
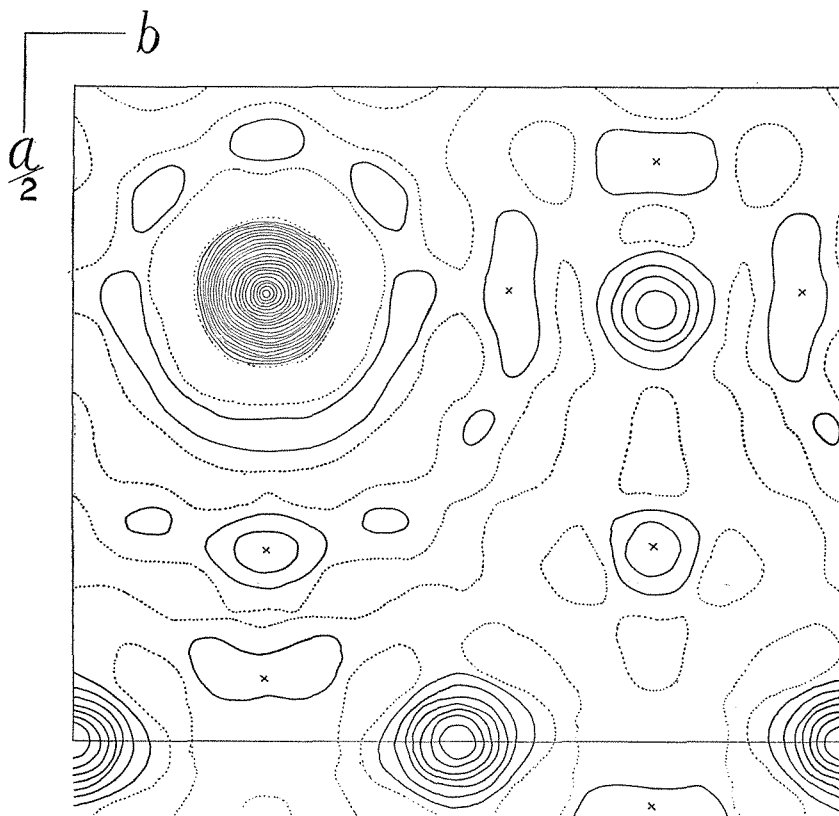

Fig. 2. Fourier map projected on the (001) plane. Contours at $10 \, eA^{-2}$. Zero contours dotted. The positions of O atoms and OH groups are indicated by crosses.

of the cell edges with the aid of Beevers and Lipson strips. The summations were repeated several times, giving necessary corrections for the atomic coordinates. For scattering factors Viervoll and Ögrim's values were applyed except for Pb atom, for which values in Internationale Tabellen were used, and the contribution of H atoms to the structure factors was neglected.

In Fig. 2 and 3 are shown the electron density projected on the (001) and (010) planes respectively, obtained in the final summations.

In order to refine the coordinates of the lighter atoms excluding the effect of diffraction ripples, difference syntheses were carried out, using the differences between F_0's and $F(Pb, Cu)$'s, where $F(Pb, Cu)$'s are the calculated structure factors to which only Pb and Cu atoms contribute. After repeating this summations, giving necessary corrections for the coordinates, the maxima in the electron density maps satisfactorily
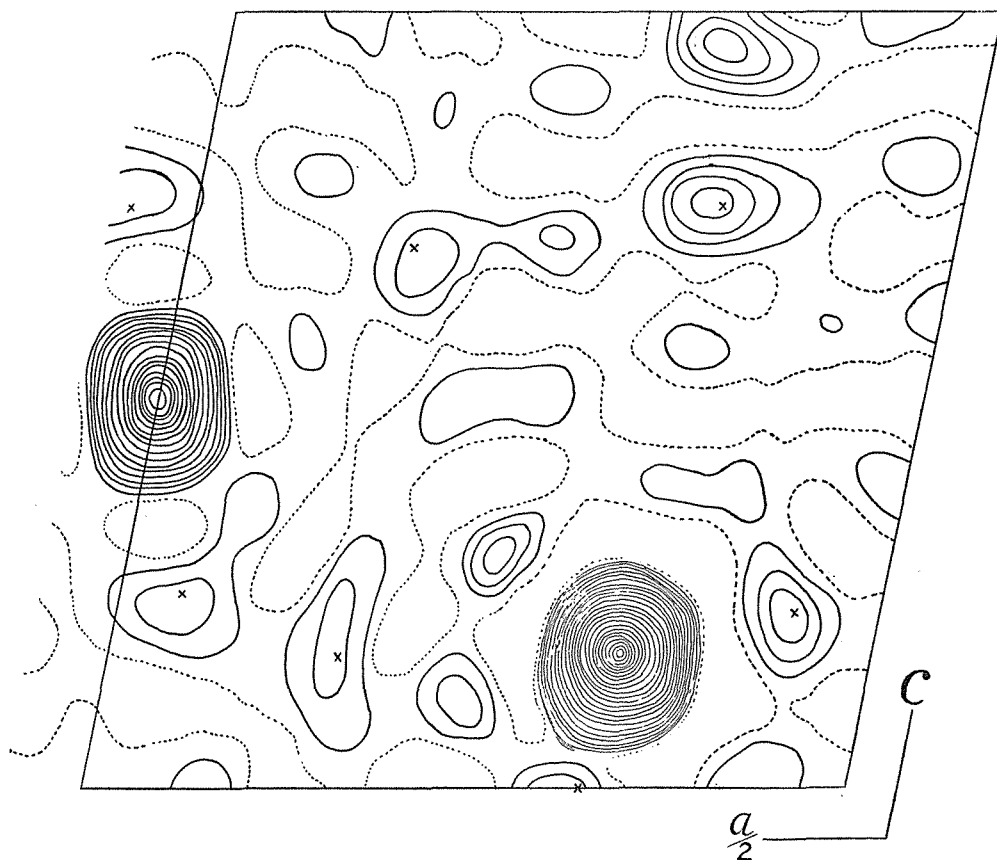

Fig. 3. Fourier map projected on the (010) plane. Contours at $10\,eA^{-2}$. Zero contours dotted. The positions of S and O atoms and OH groups are indicated by crosses.

coincided with the coordinates of S and O atoms and OH groups chosen. In Fig. 4 and 5 are shown the electron density projected on the (001) and (010) planes obtained in the final difference summations, respectively.

The coordinates of atoms found in the final syntheses are given in Table 1.

Fig. 4. The final difference synthesis projected on the (001) plane. Contours at $4\,eA^{-2}$. Zero contours dotted. The positions of Pb and Cu atoms are marked by cross and solid circles respectively.

Table 1. Coordinates of atoms.

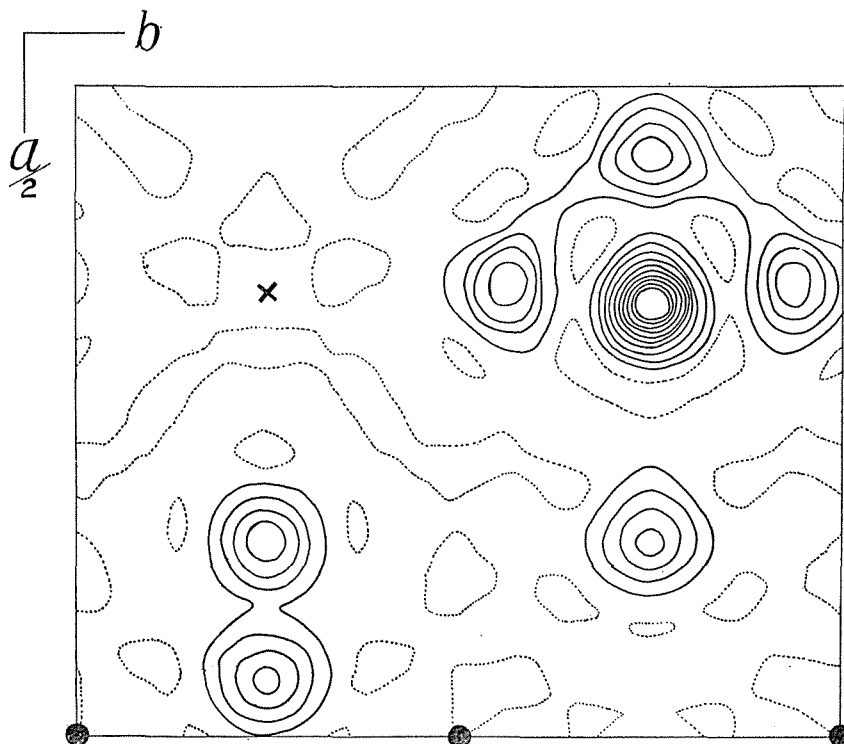| Atom	Number of atoms in a unit cell	x/a	y/b	z/c
Pb	2	0.157	0.250	0.168
Cu	2	0.500	0.000	0.500
S	2	0.830	0.250	0.998
$O_{(1)}$	2	0.944	0.250	0.774
$O_{(2)}$	2	0.654	0.250	0.834
$O_{(3)}$	4	0.846	0.060	0.248
$OH_{(1)}$	2	0.352	0.250	0.699
$OH_{(2)}$	2	0.455	0.250	0.248
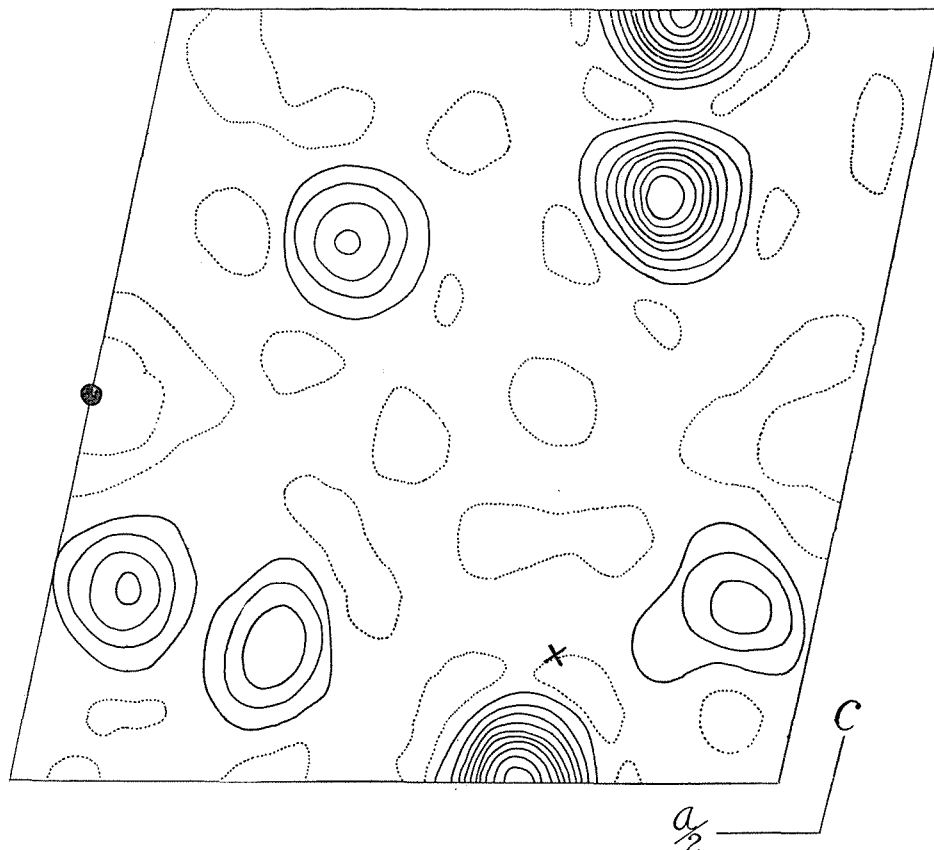
Fig. 5. The final difference synthesis projected on the (010) plane. Contours at
$4\,\mathrm{eA}^{-2}$. Zero contours dotted. The positions of *Pb* and *Cu* atoms are
marked by cross and solid circle respectively.

In Table 2 are summarized the observed and calculated structure factors, the
calculated values being calculated with atomic coordinates finally obtained and the
observed values being adjusted by multiplying factors which minimumize the relia-
bility factors.

The reliability factors are 0.195, 0.200 and 0.286 for $hk0$, $0kl$ and $h0l$ reflexions
respectively, unobserved reflexions being contained in calculations.

Structure description

In Fig. 6 is illustrated the structure of linarite.

The structure are composed of the framework of $Cu(OH)_2$ and $Pb(SO_4)$ chains
which are stretched along the *b*-axis, *Cu* atoms are situated at the center of a space

Takaharu Araki

Table 2. Observed and calculated structure factors.

hkl	F_0	F_c	hkl	F_0	F_c
100	46	45	640	96	134
200	28	−18	650	23	36
300	213	−214	660	54	−75
400	70	−83	710	53	−47
500	25	− 4	720	121	−100
600	203	182	730	27	47
700	85	58	740	54	43
800	20	12	750	37	−34
900	129	−124	810	103	−79
10,00	81	−76	820	79	47
11,00	24	−24	830	86	84
12,00	94	95	840	14	8
020	129	−143	850	65	−62
040	170	190	910	49	−51
060	72	−100	920	95	55
110	78	−94	930	48	56
120	78	−110	940	100	−103
130	83	99	10,10	29	26
140	32	27	10,20	106	117
150	67	−60	10,30	26	−27
160	74	−78	10,40	57	−70
170	48	60	11,10	81	68
210	94	−90	11,20	31	−25
220	69	93	001	51	54
230	79	100	002	52	−57
240	—	−12	003	138	−137
250	75	−62	004	19	17
260	62	64	005	46	37
270	44	63	011	95	−69
310	23	−24	012	94	−104
320	69	73	013	—	−19
330	—	26	014	102	82
340	107	−142	015	88	79
350	21	−16	021	123	−135
360	63	73	022	130	100
410	97	91	023	79	63
420	84	131	024	83	58
430	65	−88	025	96	−82
440	33	−53	031	90	89
450	50	57	032	112	94
460	69	96	033	—	2
510	111	99	034	90	−78
520	58	−68	035	68	−65
530	64	−102	041	—	38
540	—	− 1	042	19	−25
550	65	68	043	110	−113
560	51	−47	044	14	3
610	54	52	051	83	−56
620	82	−83	052	61	−76
630	24	−52	053	—	−16

Table 2. (Continued)

| hkl	F_0	F_c	hkl	F_0	F_c
054	57	69	103	43	−30
061	55	−83	$10\bar{3}$	63	−12
062	62	72	203	20	−6
063	38	51	$20\bar{3}$	—	5
071	45	60	303	109	124
101	49	11	$30\bar{3}$	63	123
$10\bar{1}$	158	202	403	—	37
201	140	−180	$40\bar{3}$	52	31
$20\bar{1}$	28	4	503	—	37
301	99	−70	$50\bar{3}$	25	−5
$30\bar{1}$	32	−5	603	90	−98
401	32	−27	$60\bar{3}$	64	−115
$40\bar{1}$	145	−167	703	36	−38
501	147	129	$70\bar{3}$	46	−47
$50\bar{1}$	29	−7	803	—	−31
601	68	64	$80\bar{3}$	31	−23
$60\bar{1}$	25	3	903	105	76
701	—	20	$90\bar{3}$	73	95
$70\bar{1}$	134	144	$10,0\bar{3}$	64	54
801	120	−112	$11,0\bar{3}$	48	40
$80\bar{1}$	44	32	104	—	38
901	61	−62	$10\bar{4}$	162	−125
$90\bar{1}$	26	12	204	126	111
10,01	22	−32	$20\bar{4}$	24	−28
$10,0\bar{1}$	95	−102	304	44	11
11,01	78	91	$30\bar{4}$	—	−33
$11,0\bar{1}$	51	−44	404	—	−4
$12,0\bar{1}$	42	−24	$40\bar{4}$	127	105
102	154	−177	504	125	−103
$10\bar{2}$	90	33	$50\bar{4}$	46	58
202	73	−36	604	46	−19
$20\bar{2}$	120	147	$60\bar{4}$	—	27
302	28	−12	704	—	3
$30\bar{2}$	48	38	$70\bar{4}$	93	−98
402	127	144	$80\bar{4}$	42	−58
$40\bar{2}$	—	27	904	—	−53
502	48	62	$10,0\bar{4}$	83	71
$50\bar{2}$	105	−149	105	103	127
602	—	10	$10\bar{5}$	—	−8
$60\bar{2}$	47	−45	205	10	25
702	119	−115	$20\bar{5}$	104	−121
$70\bar{2}$	20	−14	305	46	−25
802	57	−49	$30\bar{5}$	36	−47
$80\bar{2}$	89	106	405	90	−105
902	11	−38	$40\bar{5}$	20	−5
$90\bar{2}$	55	51	$50\bar{5}$	97	131
10,02	105	106	$60\bar{5}$	51	57
$10,0\bar{2}$	—	51	$70\bar{5}$	38	25
11,02	93	−88	$80\bar{5}$	77	−110
$12,0\bar{2}$	51	−41			
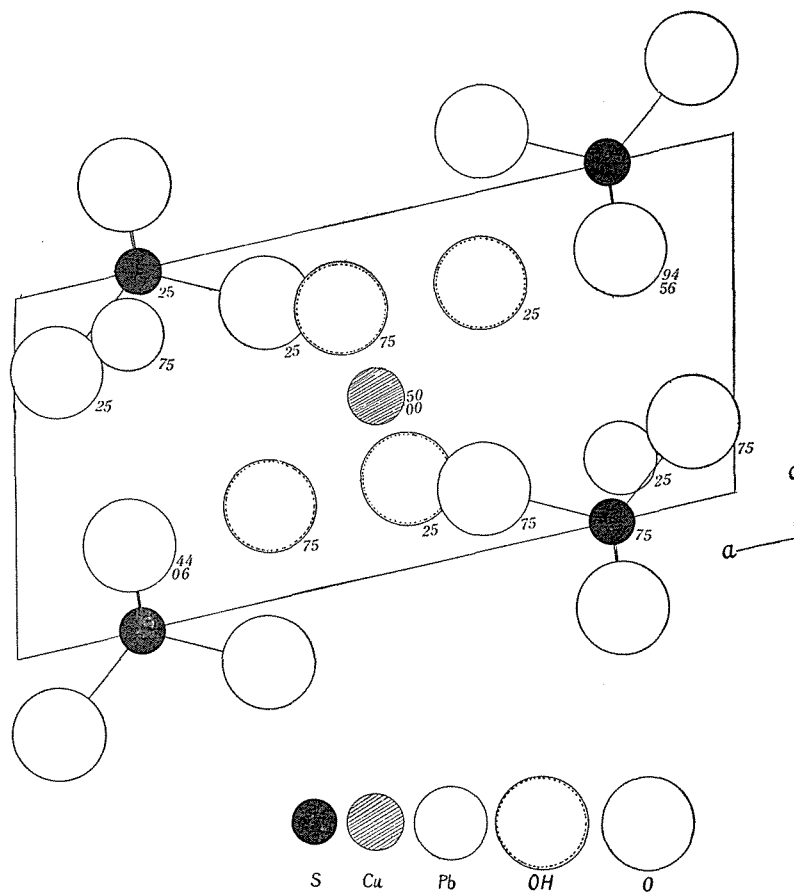
Fig. 6. The structure of linarite projected on the (010) plane.

Table 3. Interatomic distances.

Atom		Atom	Distance (Å)	Atom		Atom	Distance (Å)	Atom		Atom	Distance (Å)
S	—	O_1	1.68	Pb	—	OH_1	2.77	O_1	—	O_1''	4.11
S	—	O_2	1.71	Pb	—	OH_2	2.82	O_2	—	O_3'	3.79
S	—	O_3	1.57	Pb	—	OH_1'	3.19	O_3	—	O_3'	3.42
Cu	—	OH_1	2.20	Pb	—	O_2	3.36	O_2	—	OH_1	3.75
Cu	—	OH_2	1.82	O_1	—	O_2	2.88	O_2	—	OH_1'	2.85
Cu	—	O_2	2.37	O_2	—	O_3	2.60	O_2	—	OH_1''	3.58
Pb	—	O_1	2.45	O_1	—	O_3	2.81	O_2	—	OH_2	3.01
Pb	—	O_1'	3.02	O_3	—	O_3	2.14	O_3	—	OH_1	2.64
Pb	—	O_3	2.60	O_1	—	O_3'	2.66	OH_1	—	OH_2	2.52
Pb	—	O_3'	3.22	O_1	—	O_3''	2.70	OH_1	—	OH_2'	2.54
Pb	—	O_3''	3.39	O_1	—	O_1'	3.55	OH_1	—	OH_2''	3.36

These values imply the errors of ± 0.03Å resulted from the termination effect.

surrounded by four OH groups which are coordinated in a plane, whereas Pb atoms are situated at the positions close to two SO_4 groups in a space surrounded by five SO_4 and two OH groups.

The interatomic distances are tabulated in Table 3.

Acknowledgment

References

BERRY, L. G.: Am. Min., **36**, 511 (1951).

PALACHE, C., BERMAN, H. and FRONDEL, C.: Dana's system of mineralogy, 7th ed., **II**, 553 (1951).

ITO, T. and SAKURAI, K.: Wada's minerals of Japan, 3rd ed., 334 (1947).